TEMPORARY TECHNOLOGICAL BINDERS IN INDUSTRY

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The use of temporary technological binders in metallurgy and the refractories industry is considered and results from pilot-plant tests of new domestically produced organic binders are presented.

Keywords: binder, agglomeration, surface-active substance, structure, strength, density

Processes of compactification (extrusion, briquetting, pelletizing, agglomeration) play an enormous role in a whole series of industrial branches, in ferrous and nonferrous metallurgy, the construction materials industry, and the ceramic and refractories industry. The initial substances are generally nonplastic, for example, ores in oxide and sulfide forms, ore concentrates, nonmetalliferous natural materials, synthetic materials, and industrial dust. The function of technological binders is to assure the effectiveness of extrusion of semifinished products by lowering the internal friction in the compressed system and the friction against the wall of the mold as well as assure the coherence of the compressed system after the molding force has been removed.

In the course of molding finely dispersed powders, the unevenness of the density distribution in the body of the briquette, the internal stresses, and, consequently, fracturing as a result of the phenomenon of elastic expansion are all great. The process of improving the briquetting process proceeds basically in two directions, the first of which involves reducing the friction of the particles against the wall of the mold and the interparticle friction to assure a uniform density distribution and increase the mobility of the particles under pressure. In the second direction the design of the mold is developed to obtain large finished briquettes and assure the absence of defects in the briquettes.

From the studies carried out by P. A. Rebinder, et al. [1], it follows that the medium in which deformation of the material occurs may actively participate in the deformation process, facilitating this process if there are surface-active substances present in the medium in optimal quantities, thereby making it possible to obtain denser pressed parts under the same pressure.

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The density of stowage of friable materials in free backfilling as well as under the effect of different external factors depends not only and often not even so much on the substance of the particles of the friable material, as on the dimensions, shape, and state of the surface and structure. The cohesive forces that arise as the particles come together increase markedly by comparison with their mass (force of gravity) with decreasing dimension of the particles of a powder. Particles of small dimensions, therefore, readily form porous coagulation structures, such as unordered networks that hinder the uniform distribution of particles in a volume and their dense stowage.

Even weak van der Waals cohesive forces are sufficient to assure the strength of friable arched formations that hinder consolidation (Fig. 1). Adsorbed layers of surface-active substances or water migrate along the surface and create a two-dimensional pressure that usually proves to be higher than the strength of point contacts at the boundaries of an adsorbed layer, as a result of which the system enters a compact state with coagulation contacts (Fig. 1*b*).

In actual practice this phenomenon manifests itself in the form of different types of “fluidity” of friable materials.

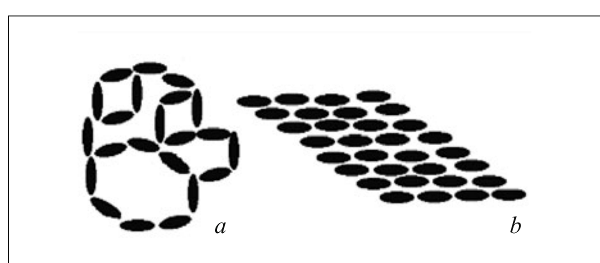

Fig. 1. Coagulation structure: *a*) primary porous structure; *b*) consolidated structure.

Powders with low fluidity poorly fill a volume. This creates difficulties when filling molds in the process of extrusion (briquetting) as well as when filling different types of vessels when transporting materials.

Studies have established a positive effect of surface-active substances on the process of consolidation of powder-like materials in the process of briquetting. A uniform distribution of a plasticizing agent on the surface of the particles is necessary; this reduces the internal friction between the particles and leads to an increase in the fluidity of the extruded mass. The density of the briquette increases to some maximum level and then decreases gradually with increasing concentration of the surface-active substances (liquid phase). The extremal nature of the variation of the density of briquettes as a function of the quantity of liquid phase is observed for most finely dispersed powders, while the density of a briquette with optimal moisture content may be twice as great as that observed if surface-active substances have not been introduced.

Thus, a high-quality temporary binder for compactification must possess two basic properties:

– surface activity, i.e., effectiveness of wetting of the surface of extruded material;

– adhesive (glueing) properties. i.e., an ability to assure cohesive strength in the course of compactification that is greater than the elastic expansion forces in the molding system.

Such a binder may be subsequently removed, i.e., it performs its function only on the stage of molding of the article. As it is completely removed in subsequent process stages, the binder does not leave ash content harmful to the properties of the article. This is the situation with the overwhelming majority of technological binders of organic composition. A technological binder may also perform its function at the stage of molding, but an organic and (or) inorganic residue may remain in the article and subsequently influence the heat-treatment process and molding of the phase composition of the article and, correspondingly, its properties. Such a binder should be considered to have been partially removed. This type of binder includes moistened clay, solutions of phosphates, sulfates, chlorides, organosilicon compounds, ash from inorganic compounds, inorganic compounds, certain organic and organometallic compounds, and other substances.

Both types of binder are used in the production of the most diverse agglomerated materials. However, the first type of temporary technological binders of organic composition is the type that is used the most often, since it enables preservation of the initial purity of a treated product and, until recently, was inexpensive and practical, which in a number of cases is a decisive circumstance.

Besides the direct problem of linking the individual particles of molded nonplastic powders into a structurally uniform body, organic and inorganic binders that have been added to a mass may perform other functions as well, for example, facilitate the retention of water, display antistatic and foam-quenching properties, etc. Organic additives that have been temporarily added to a mass are also used to stabilize aqueous slip and improve their casting properties, improve the extrusive properties of powder masses that have been subjected to semi-dry extrusion, intensify grinding of initial materials, and assure a required strength of molded billets in the moist and dry state and a required structure of the treated material.

These factors are responsible for a number of additional requirements imposed on temporary technological binders (whatever they are called):

– possess low setting time;

– assure sufficient mechanical strength, water resistance, and thermal stability of agglomerated material;

– possess the highest possible resistance to impact loads;

– not introduce harmful impurities in quantities that could have an effect on the quality of the end product;

– not worsen the quality of agglomerated material under the action of high temperatures;

– possess minimal adhesion to a molded surface;

– be of the lowest possible cost and be maximally practical and not difficult to apply;

– not create working conditions that could be harmful to the maintenance personnel, i.e., conform to public health requirements.

A large number of binders of different composition and action are now known. Independently of the class of compounds to which a technological binder belongs and the composition and kind of physico-chemical processes that occur when technological binders are added to a molded mass (and these will differ), their basic function always remains the same — to impart to a mass the property of moldability in the fabrication of an article and mechanical strength of the molded article sufficient for further operations with the mass.

A rather large number of classifications of binder substances for compactification in industry are known, though the classification that is most often used is that reflected in All-Russia State Standard 19038, according to which binders are classified according to the nature of hardening into groups as shown in Fig. 2.

1. Hydraulic binders which use different cements as the disperse phase, where the required strength is attained following addition of water

2. Polymerized and recrystallized binders in which strength is achieved in the course of recrystallization or polymerization of chemical substances or combinations of the latter with the molded materials; phosphoric acid and its salts, soluble glass, ash and gel of certain oxides, magnesial oxychloride and oxysulfide compounds, etc.

3. Coagulated binders in which strength is attained in the process of coagulation of the binder; these are refractory clays, bentonites, and organometallic compounds.

4. Organic binders which may be water-soluble (lignosulfonoates, cellulose esters, sugar, starch, polyvinyl dispersions, gelatins) or water-insoluble (oils, parafins, resins, bitumen, pitch) which assure strength as a consequence of pro-

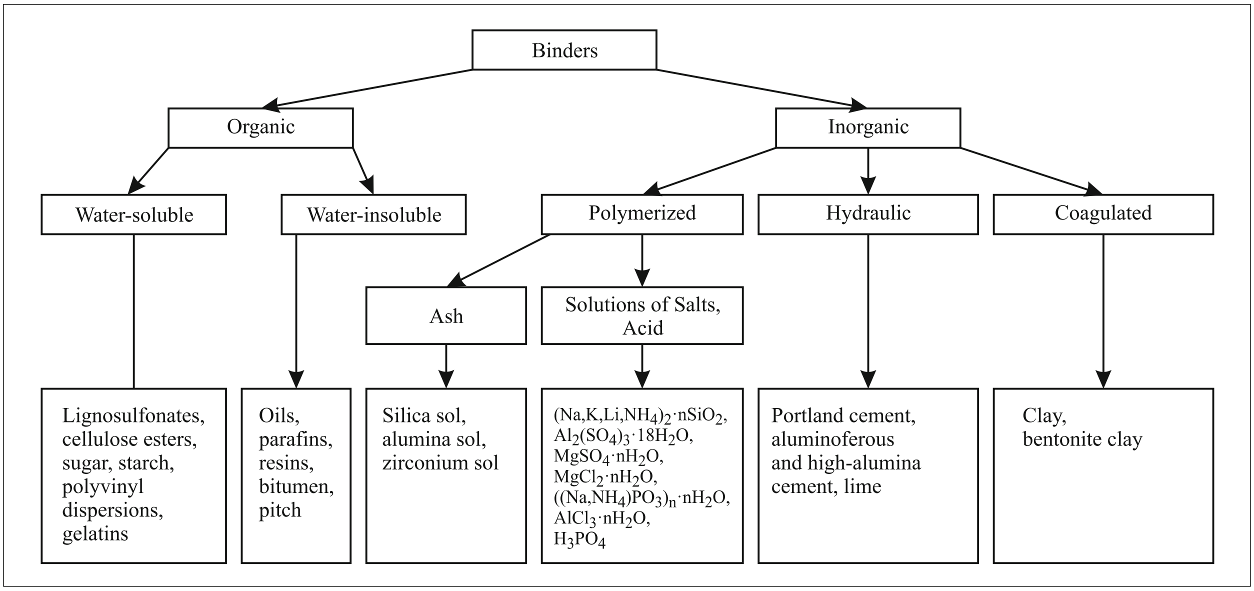

Fig. 2. Classification of temporary organic binders.

cesses of polycondensation upon removal of volatile compounds or through processes of polymerization.

The form of the binder is selected on the basis of two basic conditions: volume constancy of the molded article (sun-dried clay brick, briquette) and a required strength in a necessary temperature interval. The concentration of the binder in the molded charge is determined by compromise. On the one hand, the greater the quantity of binder, the stronger will be the article that is obtained at the ultimate temperature, while on the other hand, the binder introduces into the article additional components which at high temperatures may promote the formation of liquid phase or, upon total decomposition of the binder, tend to produce a complete loss of strength of the article. In actual practice, the quantity of binder varies from 1.5 to 15 wt. %.

In terms of chemical nature and properties, technological binders may be water-soluble or soluble only in organic liquids, may be solid or liquid, and may be of natural or synthetic origin. Most of the technological binders of organic origin that are used in industry are water-soluble solid substances. They acquire their binding properties upon dissolution in water and (or) in organic liquids. Thus, water may also be considered a component of a technological binder.

Alkaline lignosulfonates, dextrin, starch, flour, polyvinyl alcohol, water-soluble cellulose esters (methyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, etc.), sodium and ammonium alginate, sugar, etc. are all water-soluble organic binders.

Organic substances that are insoluble in water are used as temporary technological binders may be divided into liquid and solid. The nonaqueous liquids are principally drying oils, such as tung oil, linseed oil, and transformer oil, as well as different alcohols, such as methyl, ethyl, ethylene glycol, etc.

Solid organic binders used independently without solvents, for example, paraffin, and binders that are soluble in organic liquids, such as rubber and different resins and bitumens are widely used. Parafins and compounds of paraffin are the most widely used in the domestic technical-grade ceramics industry.

Of all the materials that have been enumerated, the most widely used in industry are technical-grade lignosulfonates (sulfite alcohol malt-residue), which are the wastes of the paper and pulp industry in the production of cellulose in the sulfite process, derived in purification of sulfite liquor. Lignosulfonates constitute high-molecular substances consisting of aromatic nucleic connected by means of propane radicals into nonpolar chains with polar carbonyl, carboxyl, sulfo- and hydroxo groups (Fig. 3). The presence of particular functional groups determines the specificity of the properties of lignosulfonate, which varies depending on the manufacturer and the raw material and plant utilized.

The primary wastes of sulfite cellulose production consists of alkaline (Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{3+}) salts of lignosulfonic acids and sugars in a ratio of roughly 2:1. The sugars of sulfite liquors are represented by poly- and mono-saccharides (pentoses and hexoses). The product is known as sulfite-alcohol malt residue or sulfite-yeast mash and is used precisely as an inexpensive and practical temporary binder. It combines both of the basic properties of a temporary technological binder. Thus, its organic nature assures a rather high level of surface-active substance and the presence of lignins and sugars assures high binding properties along with certain special properties, for example, sugar suppresses hydration of molded material.

With the further development of the technologies employed in treatment of the wastes generated by the paper and pulp industry, extraction of sugar from primary wastes has

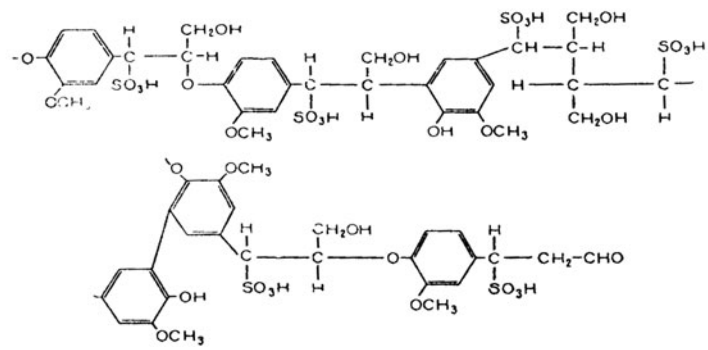

Fig. 3. Structure of lignosulfonic acid.

begun and the product that remains following extraction of the sugar has been given the commercial designation of technical-grade lignosulfonates and is now used in industry. The binding capacity of the product, like its ability to suppress hydration of materials, has fallen sharply [2].

Moreover, technical-grade lignosulfonates have fallen out of the category of inexpensive and practical wastes of production into the category of technical-grade materials that are in demand. This result is promoted by a large number of factors, the most significant of which are the following:

– an overall reduction in the capacity of the paper and pulp industry of Russia, bearing in mind that the sulfite process of producing cellulose is implemented in only 10% of all paper and pulp plants in Russia;

– an increase in the demand for temporary technological binders in industry in both Russia and neighboring countries that lack their own wood technology industry (Kazakhstan, Uzbekistan, etc.);

– an increase in the degree of treatment of wastes generated by paper and pulp plants;

– the development of technologies for the production of biofuels, including those based on the wastes of paper and pulp plants.

In summary, the cost of technical-grade lignosulfonate over the past five years has doubled (Table 1) and will only continue to grow in the future. Moreover, even in the form of sulfite-alcohol malt residue, the wastes generated by paper and pulp production possess the properties of wastes, that is, they are unstable and are obtained mainly randomly with implementation of the basic production process. At some level of development of industry, the wastes satisfy the requirements imposed on temporary technological binders. The requirements have now substantially changed. Besides the problems of "glueing" and "not yielding harmful impurities," there are also requirements associated with the distinctive features of each technology:

– suppression of hydration of the initial materials;

– production of the maximal coke residue as a high-temperature binder or as a heat source in further fusion (sintering) of the material;

– selective wettability.

It became necessary to develop special compounds with a set of their own unique properties for each particular technology. This requirement has already been satisfied by certain international manufacturers though, unfortunately, they are few in number (Table 2).

In Russia OOO Poliplast is a manufacturer of special compounds for different branches of industry. Unfortunately, the range of its products is still not very diverse, though it is actively working on expanding this range, since the market is very promising and far from saturated. Studies to expand the range of products have been underway for just over a year and have already yielded the first results. The Termoplast line of temporary technological binders has been developed

TABLE 1. Dynamics of Costs of Technical-Grade Lignosulfonates

Year	Prices for Dry Technical-Grade Lignosulfonates, rubles/ton, by month											
	1	2	3	4	5	6	7	8	9	10	11	12
2007	—	—	—	—	—	—	—	–	—	5300	5300	—
2008	7000			6000		5800	5800	5800	5800	—	5800	4500
2009	4400	5500	5800	5800	5700	7100	7600	8600	8500	8500	8800	9000
2010	10500	9200	9600	9300	9300	8700	8800	9600	10500	9600	10900	10900
2011	11800	11800	11900	11800	11700	11900	12200	12200	12200	13000	13000	13300

TABLE 2. Principal Manufacturers of Auxiliary Substances for Industry

Auxiliary Substance	Manufacturer			
	Zschimmer & Schwarz	Nisco	Rutgers Chemical AG	OOO Poliplast
Binder	LITHOPIX, LITHOSOL	POLYOX, METHOCEL	CARBORES, RAUXOLIT	TERMOPLAST
Plasticizing agent	ZUSOPLAST	SOKALAN		SP-1, S-3
Diluent	DOLAFLUX, DOLAPIX, GIESSFIX			LITOPLAST, LITOPLAST M

and laboratory and the first pilot-plant tests with different materials have been conducted.

In the area of refractories, temporary binders have been tested under the conditions of OAO Kombinat Magnezit for molding calcined periclase articles. Termoplast series binders have been added to standard magnesial charges in place of the traditional solution of technical-grade lignosulfonate using an existing technology. The results of the tests are presented in Table 3.

Termoplast-6 binder was selected from the results of laboratory studies and was subjected to pilot-plant tests under shop conditions. The obtained results are presented in Table 4.

It is evident that with the use of Termoplast series binders it becomes possible to increase the strength of both raw material and calcined articles, as well as improve their structural characteristics, such as strength and density.

In the area of briquetting of fine products in metallurgy, trial and pilot-plant tests have been conducted under the conditions of OAO Ural Mining and Metallurgical Company, OOO Mednogorsk Copper and Sulfur Combine, Division of Production of Complex Ores (PCO) (Kirovgrad, Sverdlovsk District) of OAO Ural Electrical Copper Company, and the sections of briquetting of pulverized concentrates and wastes of OAO Ural Mining and Metallurgical Combine. The charge was in the form of a mixture of copper concentrates from different manufacturers and industrial dust from different copper-smelting plants. The objective of the treatment was to obtain a briquette for use in cupolas in which more stringent requirements were imposed to ensure preservation of the dimension of the briquette before and after the roasting process.

Since decomposition in the case of overfilling of pelletized product (briquette) in the course of transportation is one of the principal destructive factors in briquetting in the mining industry, the tests were conducted according to the technique of determining strength upon knock-out adopted at OAO Ural Mining and Metallurgical Combine along with a standard technique of determining compression strength.

At the present time concentrates are briquetted with the use of a 8 – 12 wt. % solution of technical-grade lignosulfonates of density 1.25 g/cm^3 and (or) a solution of aluminum sulfate of density 1.25 g/cm^3, with briquetting wastage reaching 30%. From the results of laboratory investigations it was established that Termoplast T3 is the most optimal

TABLE 3. Results of Tests of Pilot-Plant Magnesial Articles

Binder	Compression Strength*, Mpa, after Heat Treatment at a Temperature of	
	150°C	1600°C
Technical-grade lignosulfonate	$\frac{21 - 28}{24}$	$\frac{24 - 44}{33}$
Termoplast-6	$\frac{40 - 47}{43}$	$\frac{61 - 83}{70}$
Termoplast-7	$\frac{16 - 27}{22}$	$\frac{35 - 54}{46}$
Termoplast-8	$\frac{35 - 41}{39}$	$\frac{51 - 63}{58}$
Termoplast-9	$\frac{21 - 24}{22}$	$\frac{48 - 55}{50}$
Termoplast 1-1	$\frac{19 - 21}{20}$	$\frac{55 - 57}{56}$

* The numerator represents the limiting values and the denominator, the mean value.

TABLE 4. Properties of PP and PVO Magnesial Articles (industrial batches). TLS — technical-grade lignosulfonate

Indicator	Magnitude of Indicator* with use of Binder	
	TLS	Termoplast-6
PP brand Articles		
Compression strength, MPa	$\frac{139 - 237}{178}$	$\frac{189 - 235}{211}$
Apparent density, g/cm^3	$\frac{3.08 - 3.15}{3.13}$	$\frac{3.13 - 3.19}{3.17}$
Open porosity, %	$\frac{11.9 - 13.9}{12.6}$	$\frac{10.8 - 12.5}{11.5}$
PVO brand Articles		
Compression strength, MPa	$\frac{80 - 117}{100}$	$\frac{111 - 133}{124}$
Apparent density, g/cm^3	$\frac{3.07 - 3.11}{3.10}$	$\frac{3.08 - 3.11}{3.10}$
Open porosity, %	$\frac{11.4 - 12.6}{11.7}$	$\frac{11.1 - 12.4}{11.7}$

* The numerator represents the limiting values and the denominator, the mean value.

TABLE 5. Results of Pilot-Plant Tests of Binder for Briquetting of Ore Concentrates at OAO Ural Mining and Metallurgical Company (TLS — technical-grade lignosulfonates)

Indicator	Binder Employed				
	TLS		Termoplast T3		Aluminum Sulfate
	in quantities, %				
	8	10	6	8	8
Tests at OOO Mednogorsk Copper and Sulfur Combine					
Knock-out strength, number of times	7	14	27	>30	—
Compression strength, MPa	15	—	20	26	—
Tests at Division of PCO (Kirovgrad) of OAO Ural Electrical Copper Company					
Knock-out strength, number of times	7	14	—	>15	>15
Compression strength, MPa	14	18	—	38	35

binder for briquetting the charges of copper-smelting plants; Termoplast T3 was then used in the pilot-plant tests. The results of the tests are presented in Table 5. With the use of Termoplast series binders it became possible to reduce the total quantity of binder in the charge and to increase the strength characteristics of the briquettes.

CONCLUSION

An analysis of the requirements imposed on temporary technological binders in the metallurgical and refractories industries has been presented. Comparative laboratory and pilot-plant tests of a new generation of binders manufactured by domestic producers were conducted. It was established that the use of the new generation of binders can produce an increase in the quality of the final product and reduce the specific costs incurred in its production.

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